Supporting Information

Hypercrosslinked mesoporous poly (ionic liquid)s with high ionic density for efficient CO_2 capture and conversion into cyclic carbonate

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S1. Experimental

S1.1 General

Unless specified, all reagents were commercially available and were directly used without further purification. ^{1}H and ^{13}C spectra were acquired on a Bruker DPX 500 spectrometer at ambient temperature by using DMSO or D_2O as the solvent and TMS (tetramethylsilane) as the internal reference. The IR spectra were recorded on a Nicolet 330 infrared spectrometer (Thermo Electron Corporation, USA). The textural properties were analyzed by the N_2 adsorption and desorption method (ASAP 2020, Micromeritics, USA). The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method and the pore distribution was calculated by the BJH method from desorption branches of isotherms. Thermogravimetric (TG) analysis was carried out on a NETZSCH TG 209F1 instrument. The samples were heated from 35 to 700 °C in flowing air stream (20 mL·min^{-1}) at a heating rate of 10 °C·min^{-1}. The SEM images were recorded using a HITACHI S-4800 microscope. CO_2 adsorption were analyzed by the CO_2 adsorption and desorption method (ASAP 2020, Micromeritics, USA) at 273 K. The resulting reaction mixture was analyzed by GC-mass spectrometry (GC-MS) for product identification, which was performed on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. The conversion and selectivity of products were quantified on an Agilent 7890A GC equipped with a flame ionization detector and a DB-5 column (30 m × 0.25 mm × 0.25 μm) using dodecane as the internal standard.

S1.2 Synthesis of monomers **VIm-6**, **VIm-4** and **VIm-3.**

VIm-n (n=6, 4, 3) with different ionic densities were prepared from 1,2,3,4,5,6-hexakis (bromomethyl) benzene or 1,2,4,5-tetrakis (bromomethyl) benzene or 1,3,5-tris (bromomethyl) benzene (compound **B-n'**) (n'=6, 4, 3) with 1-vinyl-1*H*-imidazole (compound **VIm**) as shown in **Scheme S1**.
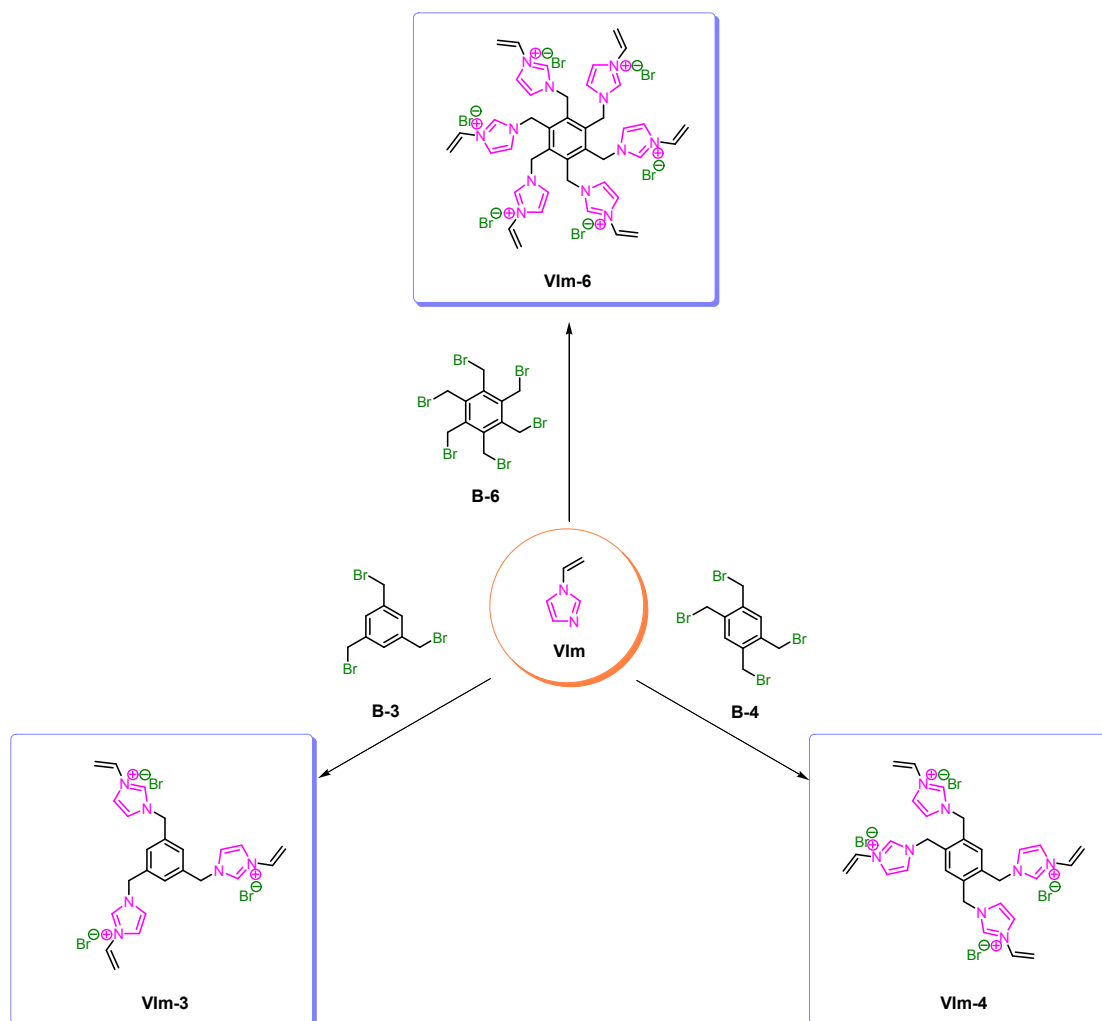
Scheme S1. Synthesis of the IL monomers with different ionic densities.
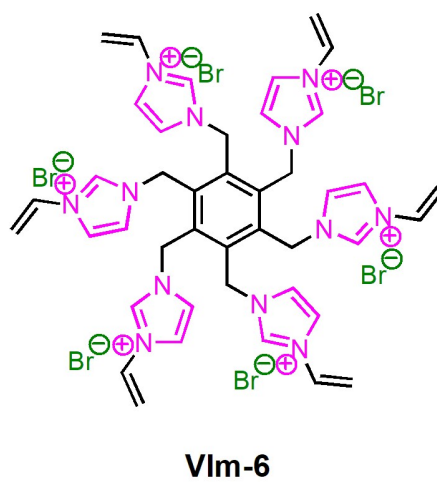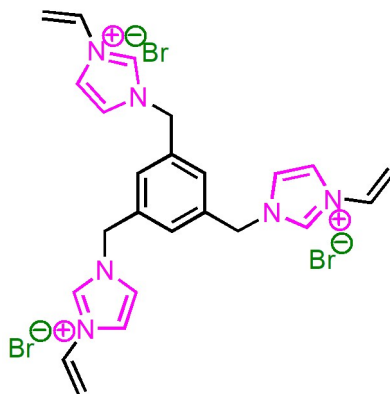

VIm-6

VIm-6 was prepared from the quaternization reaction of **B-6** with **VIm**. Compound **B-6** (6.36 g,

10 mmol) and 7.2 eq. compound **VIm** (6.78 g, 72 mmol) were added in ice cooled THF (50 mL). Then, the mixture was stirred under N_2 at 60 °C overnight. After reaction, the precipitated salt was washed by addition of 3×150 mL anhydrous ethyl acetate. After filtration, the residue was dried in a vacuum at 80 °C for 12 h to give the high purity product as brown solid in quantitative yield: ^{1}H NMR (500 M, DMSO) δ (ppm) = 5.414(dd, J = 2.0, 8.5 Hz, 6H), 5.896(s, 12H), 6.044(dd, J = 2.0, 15.5 Hz, 6H), 7.289(dd, J = 8.5, 15.5 Hz, 6H), 7.986(s, 6H), 8.193(s, 6H), 9.703(s, 6H). ^{13}C NMR (125 M, DMSO) δ (ppm) = 47.89, 109.09, 118.15, 123.72, 128.18, 135.63, 138.53.
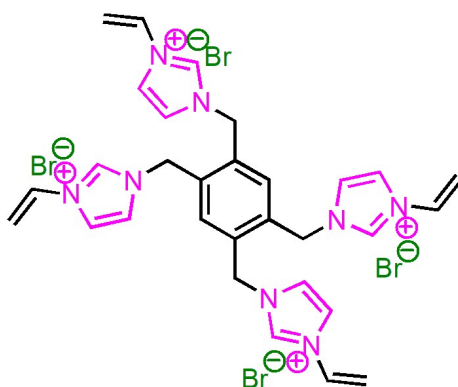
VIm-4

VIm-4 was prepared from the quaternization reaction of **B-4** with **VIm**. Compound **B-4** (4.50 g, 10 mmol) and 4.8 eq. compound **VIm** (8.84 g, 48 mmol) were added in ice cooled THF (50 mL). Then, the mixture was stirred under N_2 at 60 °C overnight. After reaction, the precipitated salt was washed by addition of 3×150 mL anhydrous ethyl acetate. After filtration, the residue was dried in a vacuum at 80 °C for 12 h to give the high purity product as brown solid in quantitative yield: ^{1}H NMR (500 M, D_2O) δ (ppm) = 5.537(dd, J = 2.5, 8.5 Hz, 4H), 5.739(s, 8H), 5.896(dd, J = 2.5, 15.5 Hz, 4H), 7.196(dd, J = 8.5, 15.5 Hz, 6H), 7.420(s, 2H), 7.648(s, 4H), 7.927(s, 4H), 9.173(s, 4H). ^{13}C NMR (125 M, D_2O) δ (ppm) = 49.94, 110.71, 120.27, 123.38, 123.43, 128.15, 134.17, 135.23.

VIm-3

VIm-3 was prepared from the quaternization reaction of **B-3** with **VIm**. Compound **B-3** (7.14 g, 20 mmol) and 3.6 eq. compound **VIm** (13.26 g, 72 mmol) were added in ice cooled THF (50 mL). Then, the mixture was stirred under N_2 at 60 °C overnight. After reaction, the precipitated salt was washed by addition of 3×150 mL anhydrous ethyl acetate. After filtration, the residue was dried in a vacuum at 80 °C for 12 h to give the high purity product as brown solid in quantitative yield: ^{1}H NMR (500 M, D_2O) δ (ppm) = 5.402(dd, J = 2.5, 8.5 Hz, 3H), 5.446(s, 6H), 5.764(dd, J = 2.5, 15.5 Hz, 3H), 7.092(dd, J = 9.0, 15.5 Hz, 3H), 7.420(s, 2H), 7.436(s, 3H), 7.493(s, 3H), 7.763(s, 3H), 9.068(s, 3H). ^{13}C NMR (125 M, D_2O) δ (ppm) = 52.31, 115.86, 123.24, 123.38, 127.15, 129.34, 134.46, 136.38.

S1.3 Preparation of PIL alcogels

In a typical preparation process for **PVIm-6** alcogel, monomer **VIm-6** (10.00 g) and AIBN (1.00 g) were dissolved in a mixture of 35 mL DMSO and 5 mL H_2O. The solution was stirred at room temperature for 2 h and then transferred into a PTFE-lined autoclave with inner-volume of 50 mL, which was then heated at 100 °C for 24 h. After reaction, a bulk gel was generated. Then, the obtained gel was collected and thoroughly washed with H_2O and ethanol to remove the remaining catalyst and unconsumed monomer. Further purification was carried out by Soxhlet extraction with ethanol for 24 h to generate **PVIm-6** alcogel. The preparation of **PVIm-3** or **PVIm-4** alcogel follows the same procedure except for the starting monomer of **VIm-3** or **VIm-4**.

S1.4 Drying process

Three different drying methods (ambient pressure drying, AD; vacuum pressure drying, VD; supercritical CO_2 drying, SCD) were used to prepare different samples. Among them, SCD method was described in detail[1, 2] as follows.
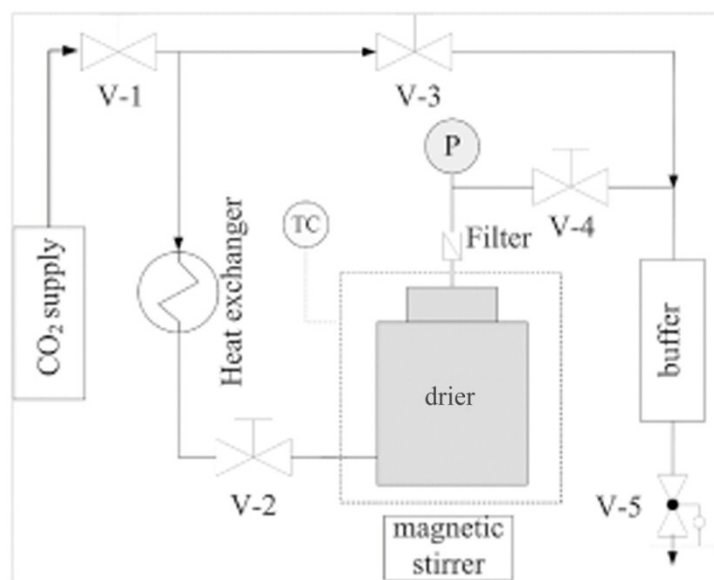

Figure S1. Schematic apparatus of the SCD process.

Figure S1 shows the schematic apparatus used for the SCD to prepare mesoporous poly (ionic liquid)s (MPILs) samples. There are three main parts: gas supply (with pressure control), drying system (drier, water bath, magnetic stirrer), and gas discharge (filter, buffer, reducing valve V-5). The SCD process was implemented at 60.0 °C and 15.0 MPa. Before the drying process, the obtained **PVIm-n** alcogel was placed in the drier. Then, CO_2 was continuously charged through the drier with a flow rate of about 1 NL/min for a period of time (2 h) until complete removal of ethanol in the **PVIm-n** alcogel. Finally, the CO_2 in the drier was discharged slowly (<0.5 MPa/min) to obtain the MPIL sample **PVIm-n-SCD**.

S1.5 Typical procedure for catalytic cycloaddition of CO_2 into cyclic carbonates

The catalytic cycloaddition of CO_2 into cyclic carbonates was carried out using a 100 mL

stainless-steel autoclave. In a typical catalytic cycloaddition (**Scheme S2**), epichlorohydrin (0.934 g, 10 mmol) and catalyst **PVIm-6-SCD** (60 mg, 0.5 mol%, according to the amount of ionic liquid monomer) were placed in autoclave equipped with a magnetic stirrer. The autoclave was carefully flushed thrice with CO_2. The reaction was carried out at specified temperature and 1 atm of CO_2 pressure for a desired period of time. After the reaction, the reactor was cooled in an ice-water bath and slowly depressurized. The reaction mixture was centrifuged to remove the solid catalyst. The qualitative analysis of product was determined by GC-MS and quantitative analysis by GC using dodecane as the internal standard. The recyclability test was conducted as follows: After the reaction, **PVIm-6-SCD** was separated by centrifugation. And then it was washed by ethyl acetate twice and anhydrous ethanol twice. After being dried by SCD, it can be directly used in the next catalytic reaction.
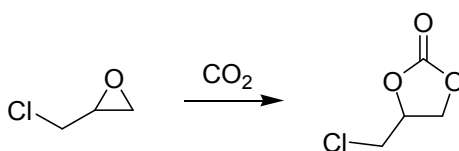
Scheme S2. CO_2 cycloaddition to epichlorohydrin

S2. Results

The SEM images of **PVIm-6-VD** and **PVIm-6-AD** are shown in **Figure S2**. N_2 sorption isotherms of samples **PVIm-6-SCD, PVIm-6-VD** and **PVIm-6-AD** are shown in **Figure S3**. The amounts of CO_2 adsorption of the three samples are shown in **Figure S4**, and their textural properties and catalytic performance comparison for the cycloaddition of CO_2 with epichlorohydrin are shown in **Table S1**. **Figure S5** shows the TG curves of **PVIm-6-SCD**. **Figure S6** shows the FT-IR spectra of **PVIm-6-SCD** and **PVIm-6-SCD-Re**. The comparisons of the textural property and CO_2 adsorption of **PVIm-6-SCD** with those of other materials are listed in **Tables S2-S4**.

Table S5 shows the reaction conditions of CO_2 cycloaddition with epichlorohydrin. **Table S6** shows the catalytic activity comparison of different heterogeneous catalysts for cycloaddition of CO_2 with epichlorohydrin. **Table S7** shows the experimental results of the reused **PVIm-6-SCD** for CO_2 cycloaddition with epichlorohydrin.

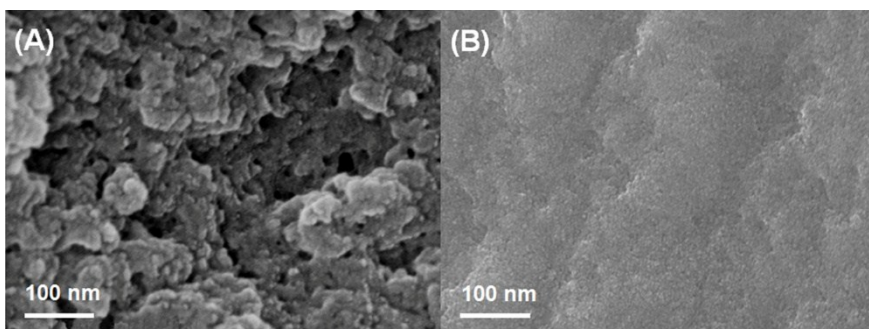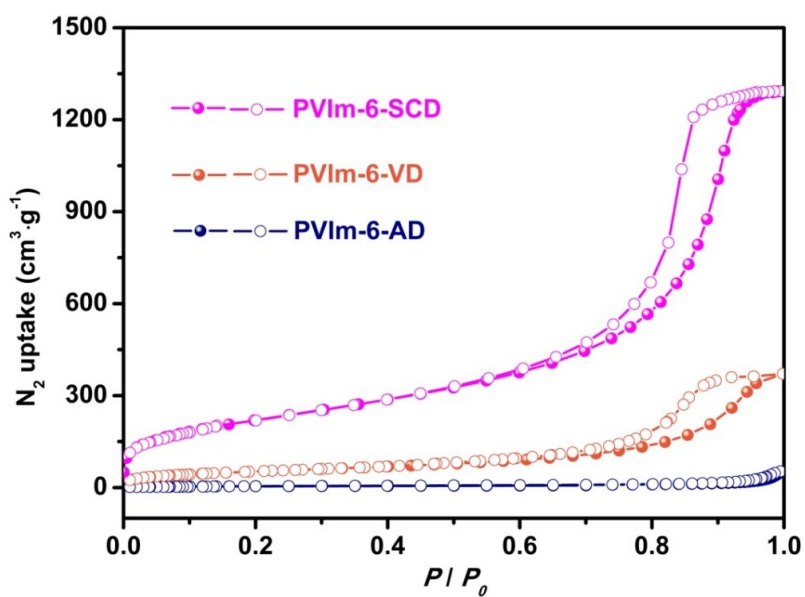**Figure S2.** SEM images of **PVIm-6-VD** and **PVIm-6-AD**.

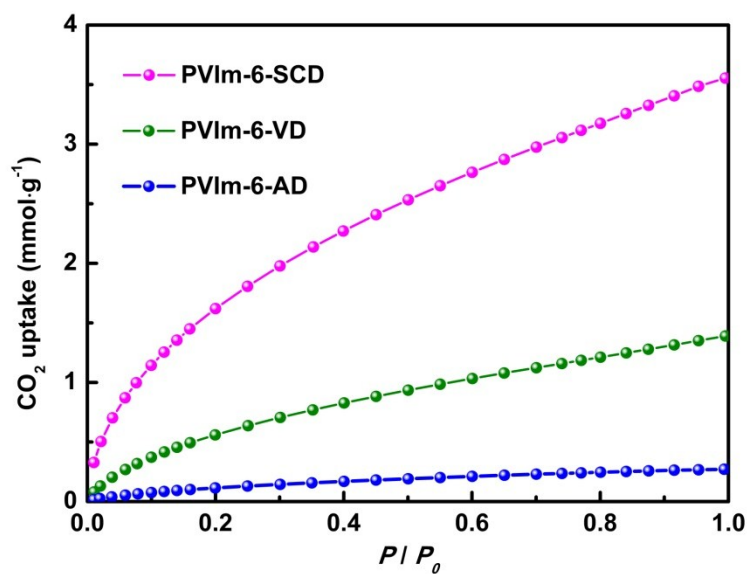**Figure S3.** N_2 sorption isotherms of samples **VIm-6-SCD, VIm-6-VD** and **PVIm-6-AD**.

Figure S4. CO_2 adsorption isotherms of samples from different drying methods (273 K, 1 atm).

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Table S1. Textural properties of the **PVIm-6** samples from different drying methods and their catalytic performance comparison for the cycloaddition of CO_2 with epichlorohydrin [a].

Entry	Catalyst	S_{BET} [b]/ $(m^2 \cdot g^{-1})$	V_P [c]/ $(cm^3 \cdot g^{-1})$	D_P [d]/ (nm)	CO_2 adsorption [e] /mmol·g^{-1}	Con. [f] / %	Sel. [f] / %
1	**PVIm-6-SCD**	797.7	2.05	9.64	3.60	98.5	99.7
2	**PVIm-6-VD**	191.5	0.57	8.4	1.31	51.7	99.5
3	**PVIm-6-AD**	--	--	--	0.23	25.2	99.9

[a] Reaction conditions: epichlorohydrin 10 mmol, catalyst 0.5 mol% (according to the amount of ionic liquid monomer), CO_2 1 atm, 50 °C, 24 h. [b] BET surface area. [c] Pore volume. [d] Average pore size. [e] At 273 K and 1 atm. [f] Conversion and selectivity were determined by GC using dodecane as internal standard.
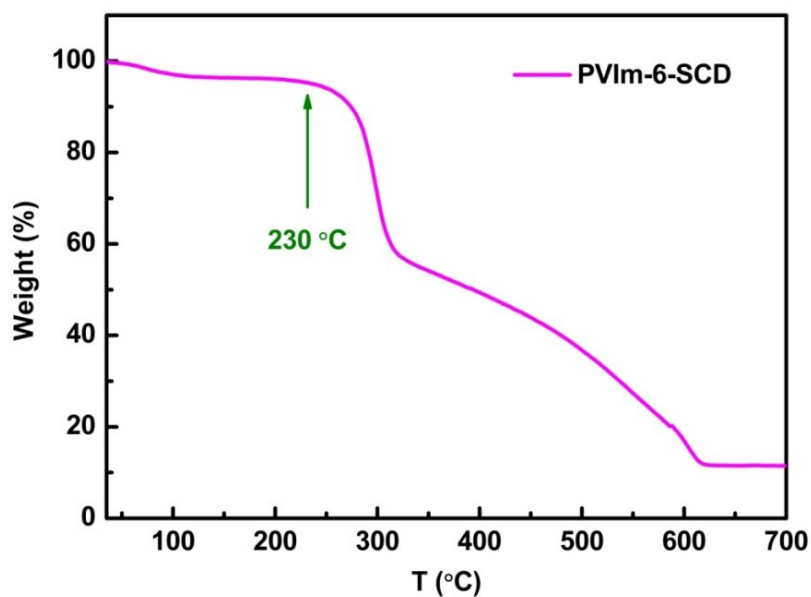
Figure S5. TG curves of **PVIm-6-SCD**.
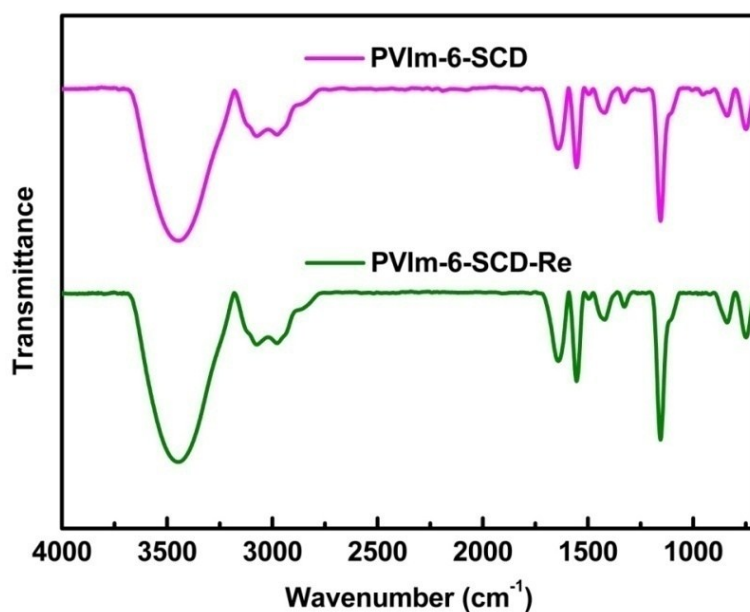
Figure S6. FT-IR spectra of **PVIm-6-SCD** and **PVIm-6-SCD-Re**.

Table S2. Textural property comparison of some typical hypercrosslinked PILs or PIPs reported in the literature with **PVIm-6-SCD**.

Year	Samples	$S_{BET}{}^a$/ (m^2·g^{-1})	$V_P{}^b$/ (cm^3·g^{-1})	$D_P{}^c$/ (nm)	Ref.
2014	**CPN-1-Br**	1455	1.0	1.6	[3]
2015	**PQP**	758	0.6	0.6-5.6	[4]
2015	**TAPOP-1**	940	0.6	0.6	[5]
2015	**Polymer 1**	1168	1.0	1.2	[6]
2016	**PCP-Cl**	755	--	0.3	[7]
2017	**cCTF**	1247	1.04	1.64	[8]
2017	**DVB@ISA**	590	0.6	1.2-2 and 2-12	[9]
2018	**PVIm-6-SCD**	797.7	2.05	9.64	**This study**

Table S3. CO_2 adsorption comparison of some typical PILs reported in the literature with **PVIm-6-SCD**.

Year	PILs	CO_2 adsorption[a] / mmol·g^{-1}	Ref.
2012	**mpPIL**	0.46	[10]
2013	**P(CMVImTf$_2$N)**	0.61	[11]
2013	**PS-CC-film/VBTMACl/ PMVPMACl/M/20%**	0.57	[12]
2014	**Poly-VI-C6**	0.50	[13]
2015	**PDMBr**	1.02	[14]
2017	**PIL-8.1.BF$_4$**	0.56	[15]
2017	**PDBA-BF$_4$-SCD**	1.23	[2]
2017	**PIP-Bn-Cl**	2.23	[16]
2018	**PVIm-6-SCD**	3.60	**This study**

[a] 273 K and 1 atm.

Table S4. CO_2 adsorption comparison of some typical hypercrosslinked nonionic and ionic polymers reported in the literature with **PVIm-6-SCD**.

Year	PILs	CO_2 adsorption[a] / mmol·g^{-1}	Ref.
2013	**TB-MOP**	4.1	[17]
2014	**CBZ**	2.1	[18]
2015	**Gal-2**	2.4	[19]
2015	**C1M2-Al**	3.4	[20]
2015	**NUT-1**	1.9	[21]
2016	**NOP-50A**	4.3	[22]
2016	**HCP-3**	2.3	[23]
2016	**PCP-Cl**	2.8	[7]
2017	**HIP-Cl-1**	3.8	[24]
2017	**NUT-6**	4.7	[25]
2018	**PVIm-6-SCD**	3.6	**This study**

Table S5. Optimization of reaction conditions of CO_2 cycloaddition[a]

Entry	Temp. / °C	time / h	Cat. [b] / mmol	Con. [c] / %	Sel. [c] / %	Yield / %
1	80	6	0.05	100.0	99.8	99.8
2	60	12	0.05	99.4	99.9	99.3
3	50	24	0.05	98.5	99.7	98.2
4	40	24	0.05	50.5	99.9	50.4
5	50	24	0.04	92.2	99.8	92.0

[a]Epichlorohydrin 10 mmol. [b]**PVIm-6-SCD** was used as catalyst and the amount was based upon the ionic liquid monomer. [c] Determined by GC using dodecane as internal standard.

Table S6. Catalytic activities of different heterogeneous catalysts for cycloaddition of CO_2 with epichlorohydrin.

Year	Catalyst	CO_2 / MPa	Temp. / °C	Time / h	Yield / %	Ref.
2007	Cross-linked-polymer-supported IL (PVBIMCl)	6	110	3	95.8	[26]
2013	Cross-linked imidazolium-based PIL	3	140	5	98	[27]
2013	Mesoporous zwitterionic PIL	1	150	8	97	[28]
2014	Fluoro-functionalized PIL	1	120	9	93	[29]
2015	Imidazolium based meso-macroporous hierarchical polymer (PDMBr)	0.1	120	12	91.3	[14]
2016	Hydroxyl-functionalized phosphonium-based ionic liquid (PNPs-HPIL-3)	2.0	140	5	97.0	[30]
2016	Porous cationic polymers (PCP-Cl)	3.0	100	12	98.0	[7]
2017	Hierarchical porous poly(ionic liquid)s (AE-PIL-Cl)	1	140	6	93	[31]
2017	Phosphonium-based porous ionic polymers (p5b)	2.5	130	15	99	[32]
2017	Imidazolinium based porous hypercrosslinked ionic polymer	1	25	96	96	[24]
2017	Imidazolium-based ionic polymer (IP3)	0.1	100	24	99	[33]
2017	Quaternary ammonium-based MPIL (PDBA-Cl-SCD)	0.1	90	6	99.3	[2]
2017	HIP-Br-2	0.1	70	96	90	[24]
2017	PIP-Bn-C	0.1	60	18	99	[16]

2018	PVIm-6-SCD	0.1	50	24	98.2	**This study**

Table S7. Experimental results from reused **PVIm-6-SCD** for CO_2 cycloaddition with epichlorohydrin. [a]

Run	Conversion [b] / %	Selectivity [b] / %	Yield/%
1	98.5	99.7	98.2
2	99.2	99.5	98.7
3	98.8	99.6	98.4
4	99.2	99.0	98.2
5	98.8	99.3	98.1
6	98.6	99.5	98.1

[a] Reaction conditions: epichlorohydrin 10 mmol, catalyst **PVIm-6-SCD** 60 mg (0.5 mol%, according to the amount of ionic liquid monomer), CO_2 1 atm, 50 °C, reaction time 24 h. [b] Determined by GC using dodecane as internal standard.

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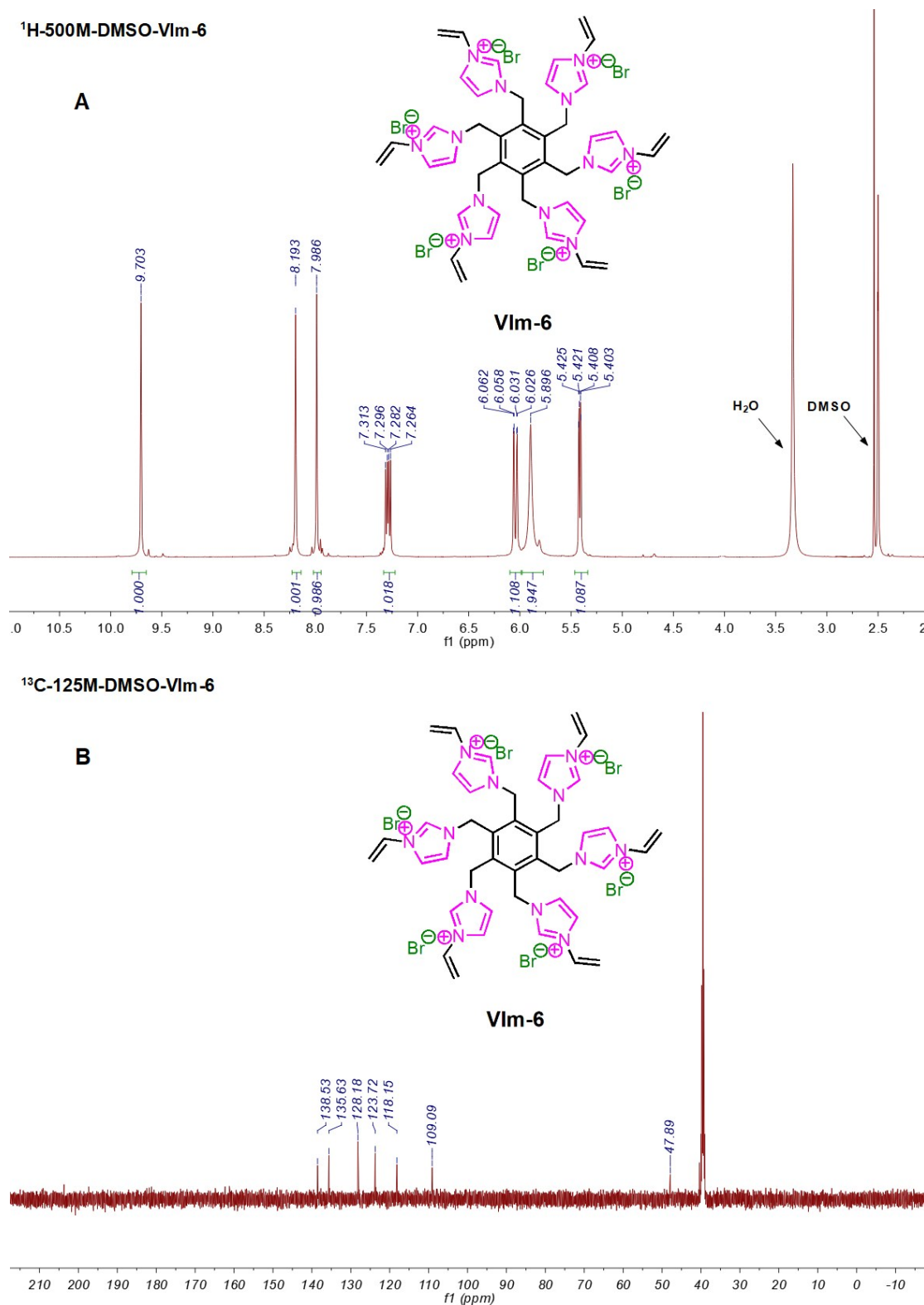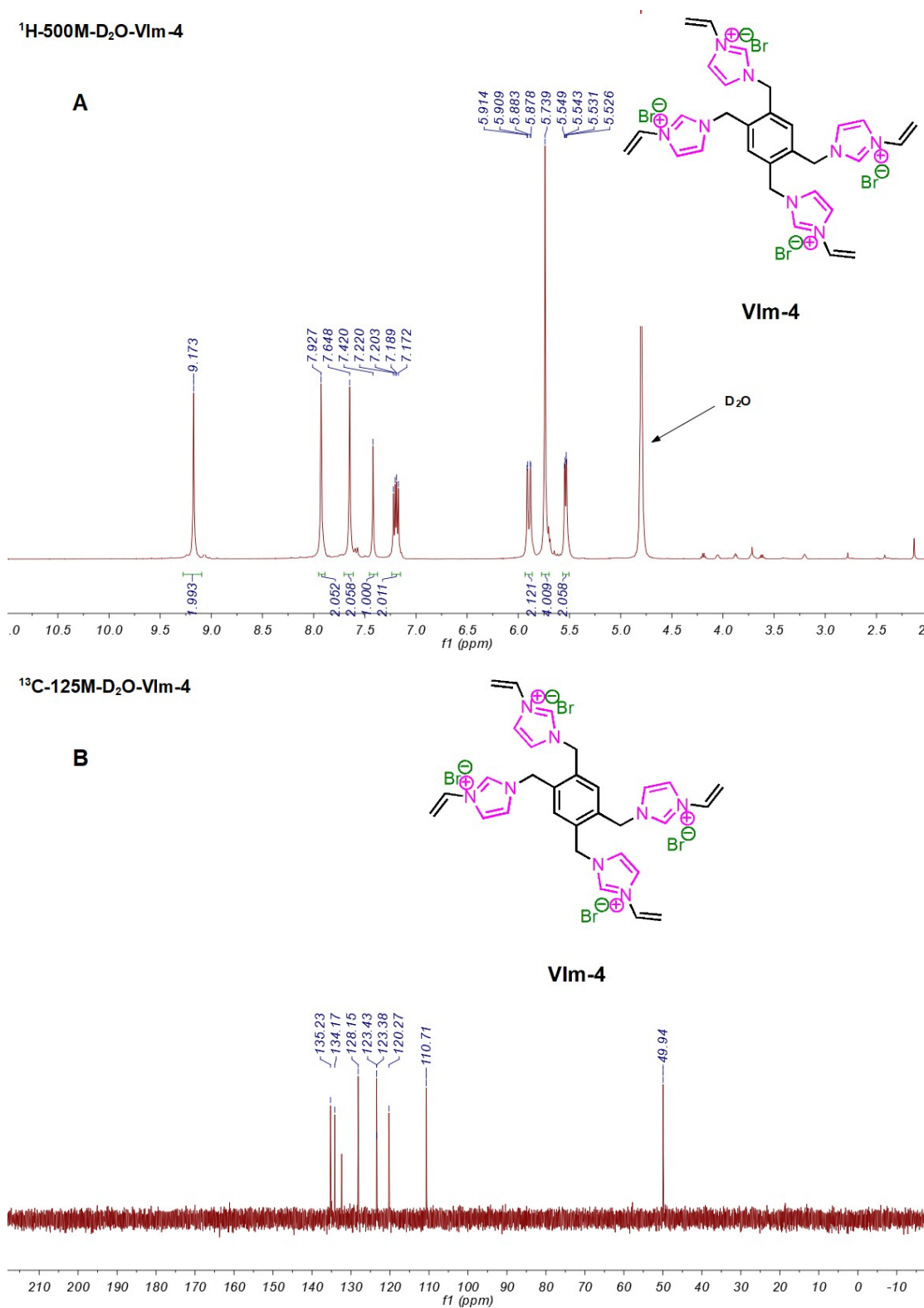
Appendix

A

Vlm-6

B

Vlm-6

Figure S7. (A) ¹H NMR and (B) ¹³C NMR of **VIm-6**.

A

Vlm-4

D₂O

B

Vlm-4

Figure S8. (A) ¹H NMR and (B) ¹³C NMR of **VIm-4**.
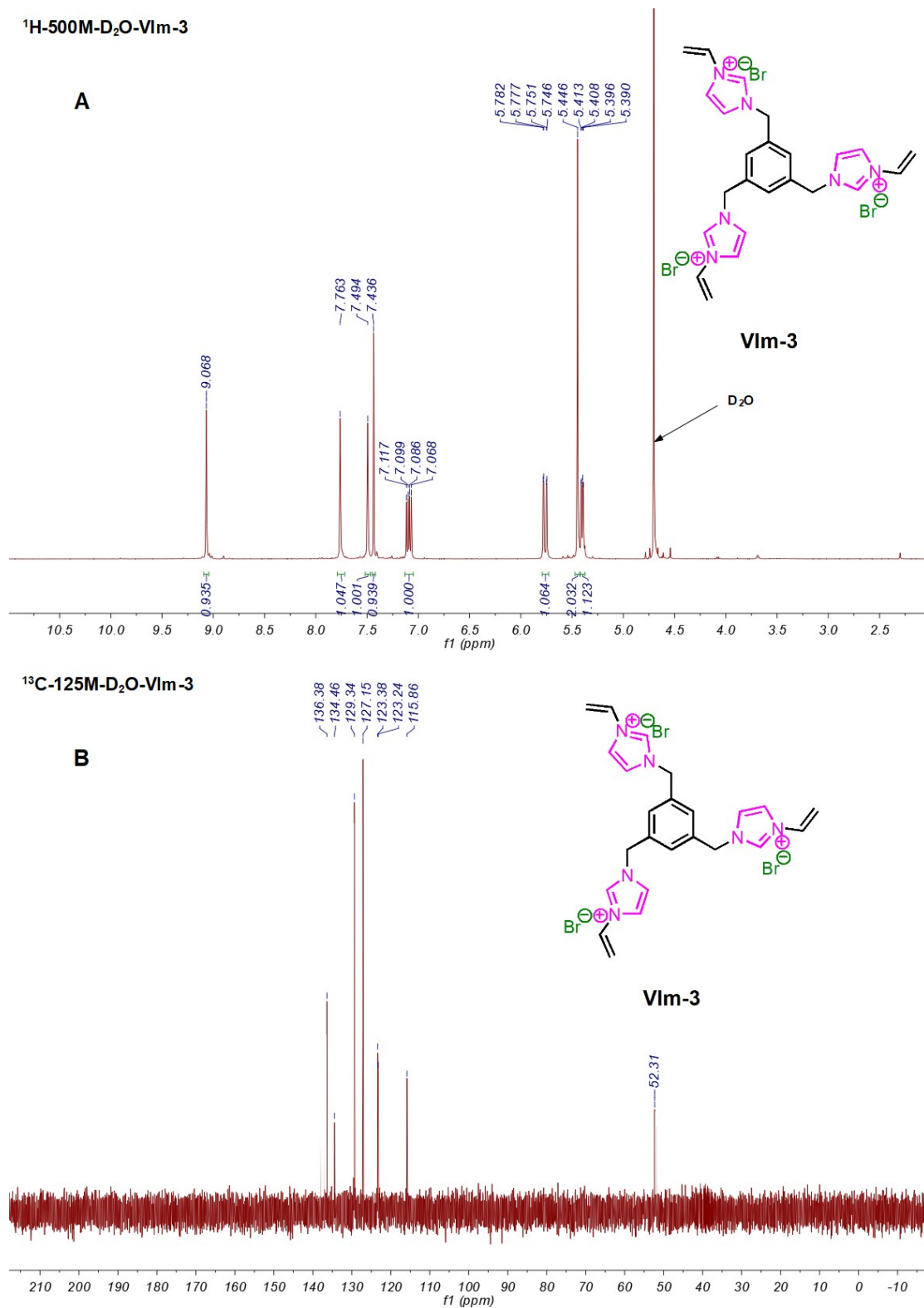
Figure S9. (A) ^{1}H NMR and (B) ^{13}C NMR of **VIm-3**.